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(54) SINGLE-ION CONDUCTING SOLID POLYMER ELECTROLYTES

EINZEL-IONEN LEITENDE FESTE POLYMERELEKTROLYTE

ELECTROLYTES DE POLYMERES SOLIDES CONDUCTEURS MONOIONIQUES

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- MACROMOLECULES, vol. 26, no. 9, 26 April
1993, WASHINGTON US, pages 2202-2208,
XP000362307 GUANG-BIN ZHOU ET AL:
"SOLVENT-FREE CATION-CONDUCTING
POLYSILOXANE ELECTROLYTES WITH
PENDANT OLIGO (OXYETHYLENE) AND
SULFONATE GROUPS"**

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Description

[0001] The present invention relates generally to novel single-ion conducting polymer electrolytes. The invention additionally relates to conductive compositions containing these novel polymers in combination with one or more plasticizers. Also within the scope of the present invention are single-ion conducting gel electrolyte film compositions, and methods of manufacturing such compositions. The invention further relates to the use of these polymers and conductive compositions in solid-state batteries, fuel cells, sensors, supercapacitors and electrochromic devices.

[0002] A number of solvent-free polymer electrolytes are known and there has been considerable interest in the potential use of such electrolytes in electrochemical devices such as solid-state batteries, fuel cells, sensors, supercapacitors and electrochromic devices. Polymer electrolytes in general have a number of desirable features, i.e., they are inherently safe in operation, they avoid the leakage and drying problems experienced with liquid compositions, and they are further relatively processable. An additional advantage of solid polymer electrolytes is their ability to deform and thus maintain interfacial contact with electrodes. Finally, polymer electrolytes may be cast in thin films to minimize resistance of the electrolyte and to reduce volume and weight.

[0003] Among the polymers which have been tested for use in solvent-free electrolyte systems are those based upon the linear-chain polyethers, poly(ethylene oxide) ("PEO") and poly(propylene oxide) ("PPO"), with associated alkali metal salts such as lithium salts. Representative PEO and PPO polymers are described by Le Nest et al., in *Polymer Communications* 28:302-305 (1987) and by Tsuchida et al., *Macromolecules* 88:96-100 (1988). However, such electrolytes display conductivity in the range of practical use (e.g., $\sigma = 10^{-5}$ - 10^{-3} S/cm) only at temperatures well above room temperature. Further, the reported linear-chain polyether electrolytes exhibit an ion transport number that is significantly lower than one, as both the anion and cation have ionic mobility and eventually account for the polymer electrolyte conductivity. Accordingly, a considerable amount of research has been focused on providing conductive solid polymer electrolytes capable of exhibiting conductivities in the range of their liquid electrolyte counterparts.

[0004] Attempts at improving the ionic conductivity of such polymer electrolytes have included the synthesis of new polymeric materials such as cation conductive phosphazene and siloxane polymers which exhibit better conductivity at room temperature than the linear-chain polyether electrolytes. In this regard, one class of polymers of interest are the polyphosphazene sulfonates as reported by Ganapathiappan et al. in both *Macromolecules* 21:2299-2301 (1988) and the *Journal of the American Chem. Soc.* 111:4091-4095 (1989); see also Chen et al., *Chem. of Materials* 1:483-484 (1984).

[0005] Other attempts at improving ionic conductivity have dealt with comb-like polymers with oligo-oxyethylene side chains anchored to a polyphosphazene, polymethacrylate or polysiloxane backbone. See, e.g., Blonsky et al., *J. Am. Chem. Soc.* 106:6854-6855 (1984), Bannister et al., *Polymer* 25:1600-1602 (1984) and Spindler et al., *J. Am. Chem. Soc.* 110:3036-3043 (1988). Since the movement of ions through the polymer matrix proceeds essentially by a free volume mechanism, polymers with flexible side chains are generally preferred. Cation transport polymer electrolytes based on cation conductive siloxane comb polymers are reported by Zhou et al., *Poly. Comm.* 30:52-55 (1989) and by Rietman et al., *J. of Poly. Sci: Part C: Polymer Letters* 28:187-191 (1990). Solid polymer electrolytes having anionic conductivity have been reported as well, see, e.g., Miyashita et al., *Macromolecules* 17:975-977 (1984).

[0006] In solid electrolytic systems, single-ion conductive polymers provide a distinct advantage over dual-ion conductive polymers (wherein both the anion and cation have mobility in the electrolyte) in that they can charge and discharge more completely (in part because DC polarization does not occur). More particularly, single-ion conducting polymer electrolytes have the capability of exclusively transporting cations, such as lithium, thereby minimizing polarization effects at the electrodes. Further, single-ion conducting electrolytes avoid the condition wherein both the dissociated cation and anion of the metal salt dissolve in the electrolyte and move toward the positive and negative electrodes at the same time, reducing the ion transportation value.

[0007] A number of single-ion conducting electrolytes have been reported. Poly(ethylene oxide)-polyelectrolyte blends--consisting of PEO mixed with an acrylate polymer having pendant sulfonate or perfluorocarboxylate groups--have been described which exhibit a lithium ion transference number close to unity. See, e.g., Bannister et al., *Polymer* 25:1291-1296 (1984). A single-ion conducting solid polymer electrolyte system comprising a solid solution having ionic species dissolved therein has also been described in U.S. Patent No. 5,102,751 to Narang et al. Further, a single-ion conducting polymer consisting of short PEO units functionalized by N-(fluoroalkylsulfonate)amido has been reported. See, e.g., Armand et al., (*Seventh International Meeting on Lithium Batteries*), May 15-20, 1994. However, each of the above-described single-ion conducting polymer systems generally exhibit low conductivity (e.g., $\sigma \leq 10^{-5}$ S/cm at 100°C) as well as low electrochemical stability.

[0008] Accordingly, while the various solid polymer electrolytes set forth in the above publications have shown promise, those materials have limitations which prevent them from practical use in, for example, high energy-rechargeable batteries and other applications in which high ionic conductivity is necessary and wherein relatively thin films of the polymer electrolyte must be prepared. As noted above, prior polymer electrolytes do not exhibit sufficient ionic conductivity, particularly at room temperature. Further, such prior polymer electrolytes have generally not exhibited desir-

able physical properties for incorporation in electrolytic devices where, frequently, thin films of these electrolytes are necessary. For example, physical limitations inherent in those polymers include polymer films which may be too sticky, the polymers may be too close to being liquid, the polymers may be too brittle, or the polymers may be too heat sensitive.

[0009] One approach to overcoming some of the above-noted problems (i.e., brittleness, low ionic conductivity) with prior polymer electrolytes has been the combination of those electrolytes with liquid electrolytes that serve as plasticizers. In this manner, a number of plasticizers have been found to be useful in enhancing the ionic conductivity of solid polymer electrolytes. See, e.g., U.S. Patent 5,102,751 to Narang et al. Additionally, gel electrolytes containing poly(vinylidene fluoride) ("PVdF") have been developed, although such polymer electrolytes generally contain conventional lithium salts which are known to behave as dual-ion conductors, reducing the cation transport values obtainable from such systems. Further, gel electrolytes containing plasticizers have been reported (see, e.g., Tsuchida et al., *Electrochemical Acta* 28 (5):591-595 (1983)); however, such electrolytes have been found to exhibit insufficiently high conductivity at room temperature. The use of PVdF copolymers to prepare gel electrolytes containing lithium salts has also been described by Gozdz et al. in U.S. Patent No. 5,296,318; however, that method did not enable preparation of homogeneous, physically strong gel electrolyte films without phasic separation of the lithium salt.

[0010] Accordingly, although some prior plasticizers have been shown to improve conductivity in solid electrolyte polymers, those compositions still suffer from serious drawbacks. In particular, prior plasticizers have been found to be too volatile, causing them to separate from the polymer electrolyte composition over a period of time. Such separation results in a decrease in the conductivity, and further, the physical properties of the polymer will likewise change; for example, the polymer might become more brittle and/or might peel from a substrate on which it has been coated.

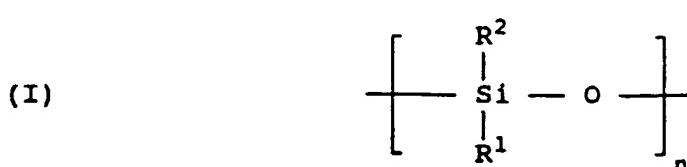
[0011] Other prior liquid electrolytes and plasticizers, such as propylene carbonate, are known to be reduced at the lithium anode or carbon anode of lithium batteries, therefore limiting battery performance. See, e.g., Arakawa et al., *J. Electroanal. Chem.* 219:273-280 (1987) and Shu et al., *J. Electrochem. Soc.* 140(4):922-927 (1993). The extent of propylene carbonate reduction is particularly severe on graphite electrodes. Although crown ethers have been used as additives in batteries to minimize such propylene carbonate reduction at the anode (see, e.g., Shu et al., *J. Electrochem. Soc.* 140(6):L101-L103 (1993) and U.S. Patent No. 5,130,211 to Wilkinson et al.), high concentrations (0.3-0.5 M) of crown ether are needed to adequately minimize electrolyte reduction. In this regard, since crown ethers are highly toxic and generally quite expensive, they are not expected to be of practical use in batteries.

[0012] WO-A-92/02571 discloses a cation conductive material comprising a polymer or a copolymer having difluoro ethylene oxide sulfonate groups providing the conductivity.

[0013] Accordingly, there remains a need to provide single-ion conductive solid polymer electrolytes capable of exhibiting conductivities in the range of their liquid electrolyte counterparts at room temperature (e.g., in the range of $\sigma \geq 10^{-3}$ S/cm at 20°C) as well as enhanced electrochemical stability. Additionally, there has remained a need to develop plasticizers for use with such polymer electrolytes that are capable of providing a plasticizing effect while also significantly enhancing the ionic conductivity of the solid polymer. Such plasticizers should not exhibit the drawbacks experienced by prior systems such as being readily volatilized away from the polymer and/or deleteriously altering the mechanical properties of the polymer.

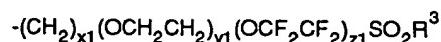
[0014] The present invention provides solid polymer electrolytes having single-ion cationic conductivity and exhibiting enhanced ambient temperature ionic conductivity. The single-ion conducting polymers as described herein include polysiloxanes, partially fluorinated polymethacrylates and poly(alkylene oxide) solid polymer electrolytes ("SPEs") which are covalently functionalized by fluoroalkysulfonate groups.

[0015] According to one aspect of the invention there is provided a single-ion conducting polymers having the structure

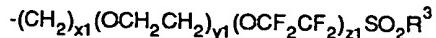


wherein:

55 R¹ and R² are individually selected from moieties having the structure



in which R³ is -OM, -N(M)SO₂CF₃ or -C(M)(SO₂CF₃)₂ and M is an alkali metal, or wherein one of R¹ and R² has the structure



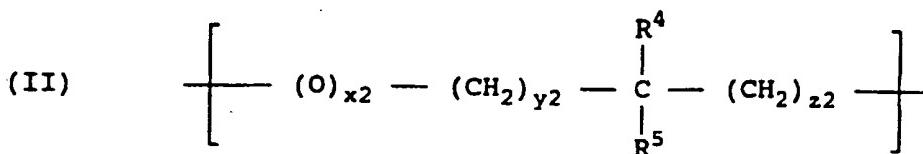
and the other is selected from hydrogen, lower alkyl, fluorinated lower alkyl, lower alkenyl, fluorinated lower alkenyl, aryl and aralkylene;

x1 and z1 may be the same or different and are integers in the range of 1 to 100 inclusive.

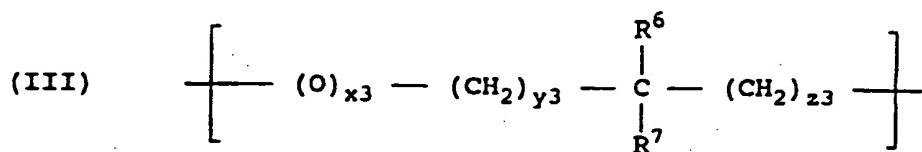
y1 is an integer in the range of 0 to 100 inclusive; and

n is an integer indicating the number of mer units in the polymer.

[0016] In another aspect the invention provides single-ion conducting co-polymers which contain first mer units having the structure



and second mer units having the structure

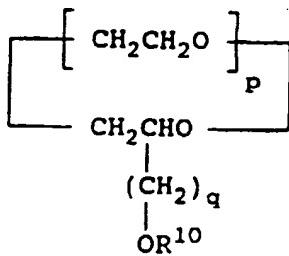


wherein:

R⁴ and R⁶ are independently selected from hydrogen, lower alkyl, lower alkoxy, -COOR⁸ and -(CH₂)_{n1}-O-R⁸ in which R⁸ is lower alkyl or fluorinated lower alkyl and n1 is an integer in the range of 1 to 6 inclusive; R⁵ is -(CH₂)_{x4}(OCH₂CH₂)_{y4}(OCF₂CF₂)_{z4}SO₃M in which M is an alkali metal; R⁷ is -(CH₂)_{x5}(OCH₂CH₂)_{y5}OCH₃ or -COOR⁹ in which R⁹ is lower alkyl or fluorinated lower alkyl; and x2, x3, x4, x5, y2, y3, y4, y5, z2, z3 and z4 may be the same or different and are integers in the range of 1 to 100 inclusive.

[0017] In a further aspects of the present invention, compositions having enhanced ambient temperature conductivity are provided, where those compositions are formed from a combination of a single-ion conducting SPE according to the present invention, and an amount of a plasticizer effective to enhance the ionic conductivity of the associated polymer. More particularly, conductive compositions containing the single-ion conducting polymers of the present invention as described above in combination with suitable medium-boiling solvents or liquid electrolytes are disclosed herein which exhibit high ambient temperature ionic conductivities and excellent physical and mechanical attributes such as high flexibility, strength and electrochemical stability. Suitable plasticizers generally feature a high dielectric constant, a medium to high boiling point, and a low viscosity.

[0018] Plasticizers which are specifically contemplated for use herein include medium-boiling solvents such as ethylene carbonate ("EC"), propylene carbonate ("PC") and combinations thereof such as a 1:1 mixture by weight of PC: EC. Other medium-boiling organic solvents which are contemplated for use as plasticizers herein include other lower alkyl carbonates such as dimethyl carbonate, diethyl carbonate and dipropyl carbonate, and glymes (e.g., dimethoxyethane ($C_4H_{10}O_2$ or "DME"), diglyme ($C_6H_{14}O_3$), triglyme ($C_8H_{18}O_4$), and tetraglyme ($C_{10}H_{22}O_5$); either alone or in combination. Cyclic carbonates may also be used as plasticizers in combination with the present polymers, e.g., functionalized cyclic ethers having the general structure



wherein:

- 15 R¹⁰ is alkyl, -(OC₂R¹¹)_m-R¹² or -(CO)OR¹³;
 R¹¹ is independently selected from H, alkyl, aryl, alkenyl, fluoro, or fluorinated alkyl;
 R¹² is H, alkyl or -(OC₂R¹¹)_m-R¹³;
 R¹³ is H or alkyl;
- 20 p is an integer in the range of 1 to 5 inclusive; and
 q is an integer in the range of 0 to 6 inclusive.

[0019] Still other plasticizers contemplated for use herein are described in co-pending U.S. Patent Application Serial No. 08/372,193, entitled "ORGANIC LIQUID ELECTROLYTES AND PLASTICIZERS" inventors Ventura et al.

[0020] In yet a further embodiment of the present invention, single-ion conducting gel electrolyte film compositions are provided wherein those films are generally formed from a combination of a single-ion conducting SPE as described above with a plasticizer and a suitable amount of poly(vinylidene fluoride) for enhancing the mechanical strength of the resulting gel electrolyte composition. In this manner, the single-ion conducting SPEs of the present invention exhibit desirable physico-mechanical properties in that they may be formulated in thin but nevertheless highly conducting films having desirable physical properties such as enhanced mechanical strength and lack of stickiness.

[0021] According to the invention, there is further described a method of manufacturing single-ion conducting electrolyte films and other conductive compositions. Generally, such a method will involve a hot press technique for forming films; however, depending on the amounts of various components incorporated into the compositions, waxes and gels may be prepared as well.

[0022] In still another embodiment of the present invention, the SPEs may be used in the formulation of solid-state electrochemical devices such as fuel cells, supercapacitors, electrochromic devices and sensors, or in a battery such as in a solid state lithium battery. In this regard, a solid-state battery comprising a positive electrode, a negative electrode and a single-ion conducting solid polymer electrolyte as described above is disclosed herein.

[0023] In yet a further embodiment of the invention, the presently described SPEs may be used in combination with plasticizers to form thin film SPEs; and, optionally, PVdF or an alternative material may be added in order to improve the SPE film mechanical strength. Accordingly, also provided herein are solid-state batteries comprising a positive electrode, a negative electrode and a single-ion conducting polymer electrolyte film according to the invention. With the subject SPE films, solid-state batteries such as a Li_xC₆/SPE/LiCoO₂ battery may be fabricated having enhanced conductivity and rechargability.

Brief Description of the Figure

[0024] FIG. 1 is a diagram illustrating ranges of components in a composition containing a single-ion conducting polymer electrolyte, a plasticizer, and PVdF, for forming films, waxes and gels.

Detailed Description of the Invention Definitions:

[0025] Before describing the present invention in detail, it is to be understood that this invention is not limited to particular salts, methods of synthesis, or solvents as such may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0026] It must be noted that, as used in this specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to "a plasticizer" includes mixtures of plasticizers.

[0027] In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings:

[0028] The term "polymer" is intended to include both oligomeric and polymeric species, i.e., compounds which include two or more monomeric units, which may be a homopolymer or a copolymer. When a single generic structure is shown, e.g., as in formula (I), it is to be understood that the polymers described may contain two or more different monomeric units represented by the single generic structure. A "conductive polymer" is one which possesses conducting as opposed to insulating electrical-transport properties.

[0029] The term "homopolymer" intends a polymer incorporating a single species of monomer units. By contrast, the term "copolymer" refers to a polymer constructed from two or more chemically distinct species of monomer units in the same polymer chain. A "block copolymer" is a polymer which incorporates two or more segments of two or more distinct species of homopolymers or copolymers.

[0030] The term "alkyl" as used herein refers to a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, octyl, decyl, tetradecyl, hexadecyl, eicosyl and tetracosyl. Preferred alkyl groups herein contain 1 to 12 carbon atoms. The term "lower alkyl" intends an alkyl group of one to six carbon atoms. The term "fluorinated lower alkyl" intends an alkyl group of one to six carbon atoms in which at least one hydrogen atom, and optionally all hydrogen atoms, are replaced with fluorine atoms.

[0031] The term "alkenyl" refers to a branched or unbranched hydrocarbon chain containing from 2 to 24 carbon atoms and at least one double bond. "Lower alkenyl" refers to an alkenyl group of 2 to 6, more preferably 2 to 5, carbon atoms. The term "fluorinated lower alkenyl" intends an alkenyl group of one to six carbon atoms in which at least one hydrogen atom, and optionally all hydrogen atoms, are replaced with fluorine atoms.

[0032] The term "alkoxy" as used herein intends an alkyl group bound through a single, terminal ether linkage; that is, an "alkoxy" group may be defined as -OR where R is alkyl as defined above. A "lower alkoxy" group intends an alkoxy group containing one to six, more preferably one to four, carbon atoms.

[0033] The term "aryl" as used herein refers to a monocyclic aromatic species of 5 to 7 carbon atoms, and is typically phenyl. Optionally, these groups are substituted with one to four, more preferably one to two, lower alkyl, lower alkoxy, hydroxy, and/or nitro substituents.

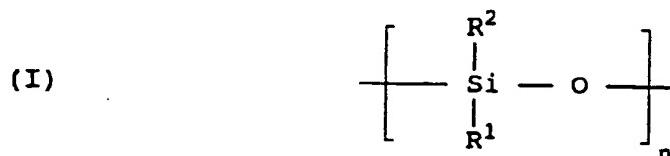
[0034] The term "aralkylene" is used to refer to moieties containing both alkylene and monocyclic aryl species, typically containing less than 12 carbon atoms in the alkylene portion, and wherein the aryl substituent is bound to the structure of interest through an alkylene linking group. Exemplary aralkylene groups have the structure -(CH₂)_j-Ar where j is an integer in the range of 1 to 6.

[0035] "Halo" or "halogen" refers to fluoro, chloro, bromo or iodo, and usually relates to halo substitution for a hydrogen atom in an organic compound. Of the halos, fluoro is typically preferred.

[0036] "Optional" or "optionally" means that the subsequently described circumstance may or may not occur, and that the description includes instances where said circumstance occurs and instances where it does not. For example, the phrase "optional covalent bond" means that a covalent bond may or may not be present and that the description includes both the instance when the covalent bond is present and the instance when the covalent bond is not present.

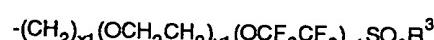
The Novel Compounds:

[0037] In one embodiment of the invention, there are provided a number of polysiloxane single-ion conducting solid polymer electrolytes covalently functionalized by fluoroalkylsulfonate groups. More particularly, there are provided polysiloxane SPEs having the general structure as shown in Formula I

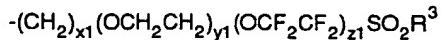


wherein:

R¹ and R² are individually selected from moieties having the structure



in which R³ is -OM, -N(M)SO₂CF₃ or -C(M)(SO₂CF₃)₂ and M is an alkali metal, or wherein one of R¹ and R² has the structure

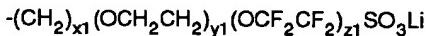


5 and the other is selected from hydrogen, lower alkyl, fluorinated lower alkyl, lower alkenyl, fluorinated lower alkenyl, aryl and aralkylene;
 x1 and z1 may be the same or different and are integers in the range of 1 to 100 inclusive;
 y1 is an integer in the range of 0 to 100 inclusive; and
 n is an integer indicating the number of mer units in the polymer, generally although not necessarily providing the
 10 polymer with a (weight average) molecular weight in the range of 10,000 to 3,000,000, more typically in the range of 100,000 to 1,000,000.

[0038] In preferred polysiloxane SPEs having the structure shown in Formula I, M is lithium.

[0039] In one group of particularly preferred polysiloxane SPEs having the structure of Formula I, R¹ and R² are the same moiety having the structure

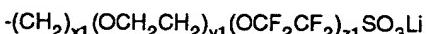
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20 in which x1 and z1 may be the same or different and are integers in the range of 1 to 100 inclusive, and y1 is an integer in the range of 0 to 100 inclusive;

[0040] In another group of particularly preferred SPEs encompassed by Formula I, R¹ is a moiety having the structure

25



in which x1, y1 and z1 are as defined above, and R² is selected from hydrogen, lower alkyl, fluorinated lower alkyl, lower alkenyl, fluorinated lower alkenyl, aryl and aralkylene.

[0041] In still another group of particularly preferred SPEs having the structure of Formula I, R¹ and R² are the same moiety having the structure

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in which x1, y1 and z1 are as defined above.

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[0042] Additional particularly preferred SPEs of Formula I are wherein R¹ is a moiety having the structure



40

R² is selected from hydrogen, lower alkyl, fluorinated lower alkyl, lower alkenyl, fluorinated lower alkenyl, aryl and aralkylene, and x1, y1 and z1 are as defined above.

[0043] Still other particularly preferred SPEs having the structure of Formula I are wherein R¹ and R² are the same moiety having the structure

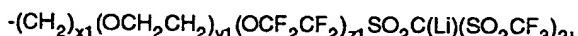
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in which x1, y1 and z1, again, are as defined above.

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[0044] Yet an additional group of particularly preferred SPEs according to Formula I are those wherein R¹ is a moiety having the structure



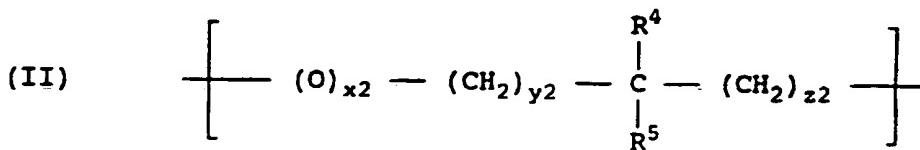
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R² is selected from hydrogen, lower alkyl, fluorinated lower alkyl, lower alkenyl, fluorinated lower alkenyl, aryl and aralkylene, and x1, y1 and z1 are as defined earlier.

[0045] In addition to the polysiloxane family of SPEs provided herein, i.e., those polymers having the structure of Formula I, a number of polymethacrylates and poly(alkene oxides) covalently functionalized by fluoroalkylsulfonate

groups have been found to be useful as well. More particularly, there are provided a number of copolymeric SPEs containing first mer units having the structure (II)

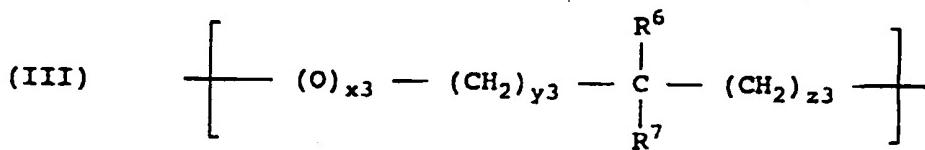
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and second mer units having the structure (III)

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wherein:

25 R^4 and R^6 are independently selected from hydrogen, lower alkyl, lower alkoxy, $-COOR^8$ and $-(CH_2)_{n1}-O-R^8$ in which R^8 is lower alkyl or fluorinated lower alkyl and $n1$ is an integer in the range of 1 to 6 inclusive; R^5 is $-(CH_2)_{x4}(OCH_2CH_2)_{y4}(OCF_2CF_2)_{z4}SO_3M$ in which M is an alkali metal; R^7 is $-(CH_2)_{x5}(OCH_2CH_2)_{y5}OCH_3$ or $-COOR^9$ in which R^9 is lower alkyl or fluorinated lower alkyl; and $x2, x3, x4, x5, y2, y3, y4, y5, z2, z3$ and $z4$ may be the same or different and are integers in the range of 1 to 100 inclusive.

30

[0046] As with the polymers of Formula I, preferred copolymers containing mer units (II) and (III) are wherein M is lithium. Also, these copolymers will generally have a (weight average) molecular weight in the range of 10,000 to 3,000,000, more typically in the range of 100,000 to 1,000,000.

35 **[0047]** A number of preferred copolymers useful as SPEs may be identified. A first group of such copolymers are wherein R^4 and R^6 are hydrogen or lower alkyl, and R^7 is $-(CH_2)_{x4}(OCH_2CH_2)_{y4}OCH_3$, with $x4$ and $y4$ defined as above.

[0048] Another group of particularly preferred copolymers useful as SPEs are wherein R^4 and R^7 are independently $-COOR^8$ and R^6 is hydrogen or lower alkyl.

40 **[0049]** The polymers of the invention may be prepared using conventional techniques well-known to those skilled in the art of synthetic organic chemistry or which may be found in the relevant texts such as in Kirk-Othmer's Encyclopedia of Chemical Technology, in House's Modern Synthetic Reactions, in C.S. Marvel and G. S. Hiers' text, ORGANIC SYNTHESIS, Collective Volume 1, or the like. Synthesis of representative polymers is exemplified below.

Manufacturing Methods:

45 **[0050]** A preferred method of manufacturing conductive compositions containing the novel electrolytes is a hot-press technique for forming films. Such a method typically involves: (a) forming a gel electrolyte composition by combining (i) a single-ion conducting SPE of the invention (i.e., a polysiloxane of Formula (I) or a copolymer containing mer units (II) and (III)), with (ii) an effective amount of plasticizer for enhancing the ionic conductivity of that SPE and (iii) an amount of PVdF or an alternative material effective to enhance the mechanical strength of the composition; (b) heating 50 the resulting combination at a temperature and for a time effective to form a fluid solution; (c) pressing the fluid solution; (d) cooling the solution; and (e) releasing the film so provided.

55 **[0051]** If waxes or gels are preferred, rather than films, the relative quantities of components can be adjusted to provide these alternative forms of conductive compositions. Reference may be had to Figure 1, in which it may be seen that compositions containing less electrolyte will generally form a gel, compositions containing slightly more electrolyte will generally form a wax, and compositions containing even more electrolyte will form a film. Alternative methods of manufacturing such conductive compositions will be readily apparent to those skilled in the art, or may be deduced from the relevant literature.

Industrial Applicability:

[0052] Conductive compositions formulated with the novel single-ion conducting solid polymer electrolytes are useful in a variety of contexts. An important utility is in the fabrication of batteries. Solid-state batteries formulated with the novel electrolyte polymers comprise a positive electrode, or anode, a negative electrode, or cathode, and the single-ion conducting polymer electrolyte. The anode is usually a carbon-based material such as petroleum coke or graphite. Alternatively, lithium metal may be used as the anode, or intercalating metal oxides such as tungsten or iron oxides. The cathode is generally of a lithium-containing material such as LiCoO₂, LiMn₂O₄ or LiNiO₂; however, alternative materials could be used as well, e.g., V₆O₁₃.

5 [0053] It will be appreciated that conductive compositions formulated with the novel electrolyte materials of the invention are also useful in the fabrication of fuel cells, sensors, supercapacitors, and electrochromic devices using manufacturing techniques well known to those skilled in the art, or readily available in the relevant literature.

10 [0054] The following examples are intended to provide those of ordinary skill in the art with a complete disclosure and description of how to make and use the materials of the invention, and are not intended to limit the scope of what 15 the inventors regard as their invention in any way. Efforts have been made to ensure accuracy with respect to numbers used (e.g., amounts, and temperatures), but some experimental error and deviation should, of course, be allowed for. Unless indicated otherwise, parts are parts by weight, temperatures are in degrees centigrade, and pressure is at or near atmospheric.

20 **Experimental**

Equipment and Measurement Techniques:

25 [0055] Conductivities of the polymers were evaluated by AC impedance spectroscopy. In this regard, a film of the dried polymer electrolyte was sandwiched between two stainless steel blocking electrodes, each having an area of 0.7854 cm². The thickness of the polymer film, which typically varied between 0.51 mm and 1.02 mm, was measured with a micrometer. An assembly, composed of a blocking electrode-polymer sandwich cell inside a Delrin cup, was transferred to a vacuum chamber that had provision for heating and applying a constant pressure of 65-97 lb/in₂ (448 - 669 kPa) across the polymer film. Electrodes were connected to a potentiostat (PAR 173) operating in the galvanostatic mode.

30 [0056] The cell was then perturbed with a small AC signal generated by a Solartron 1250 Frequency Response Analyzer, and the real and imaginary components of the cell impedance were measured as a function of frequency at each of the desired temperatures. The setup was allowed to stabilize overnight after the temperature was changed. 35 The AC impedance data were plotted in both the Nyquist and Bode planes to identify the high frequency relaxation arising due to the polymer electrolyte. Typically, the frequency of the AC signal was scanned from 65 KHz down to 10 mHz. The intercept at the real axis of the high frequency relaxation was assumed to represent the resistive component of the polymer electrolyte impedance. This was then converted to the resistivity of the polymer (the thickness and the area of the polymer films were known). The reciprocal of resistivity gave the conductivity, a, having units of Ω⁻¹cm⁻¹. In cases where high frequency relaxation occurred above 65 KHz, a Hewlett-Packard 4192A Impedance Analyzer was 40 used to measure the polymer electrolyte resistance. This instrument has a frequency range capability of 13 MHz to 5 Hz.

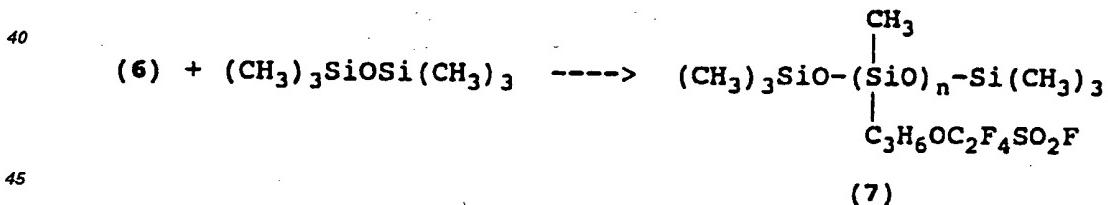
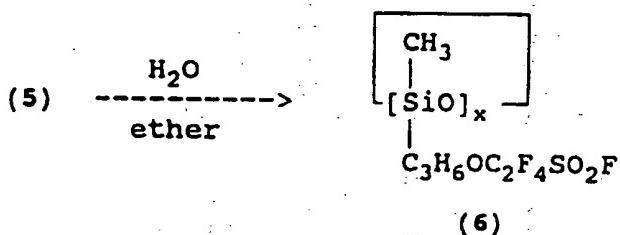
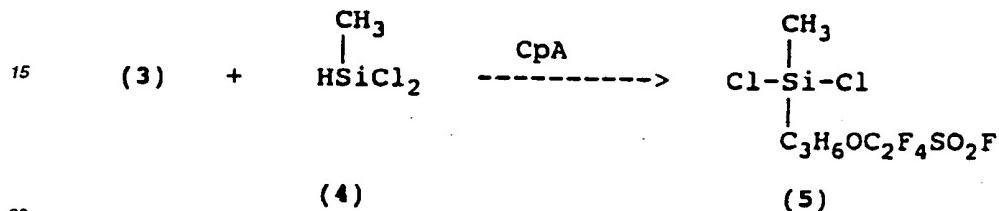
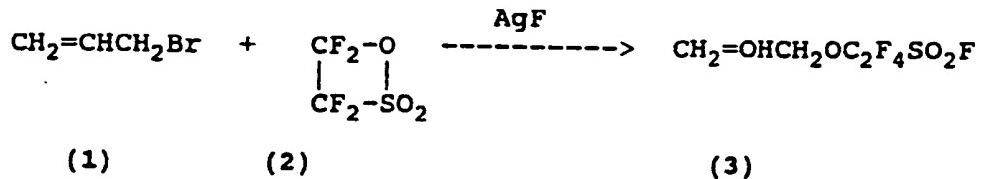
Preparation of Polymer Films:

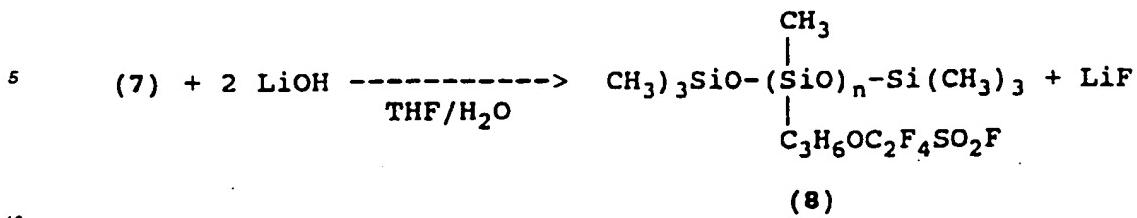
45 [0057] Solutions of polymer films were prepared by dissolving a known quantity of polymer in dry solvent. For conductivity measurements, the polymer solution was added dropwise into the Delrin cup to cast a film. The film was then dried for 3 days in a glass vacuum apparatus at 120°C at <0.01 torr (1.33 Pa). Film thickness was measured using a micrometer.

50 **Example 1**

Preparation of Polymethylsiloxane with C₃H₆OC₂F₄SO₃Li Pendant Group

55 [0058] Polymethylsiloxane carrying a C₃H₆OC₂F₄SO₃Li pendant group was synthesized as according to the following scheme and procedures:





(a.) Preparation of Fluorosultone (2):

In a 500-ml Parr pressure reactor equipped with a magnetic stirrer, 50 ml of fresh sulfur trioxide was prepared by distillation of fuming sulfuric acid. Under stirring, tetrafluoroethylene was introduced continuously at the pressure of 30 psi (207 kPa). Exothermic reaction took place. The volume of the liquid content increased gradually as the reaction proceeded. At the end of the reaction, the crude product was purified by distillation. A colorless liquid product was collected at the temperature of 42–43°C. 162.9 g fluorosultone (2) was obtained.

(b.) Preparation of (3):

In a 250-ml 3-neck flask equipped with a magnetic stirrer and covered with aluminum foil, 63.44 g (0.50 mol) of silver fluoride and 100 ml of anhydrous diglyme were combined. The flask was cooled to -78°C and 90.04 g (0.50 mol) of fluorosultone (2) was added dropwise. A clear solution was produced after 1 hr at room temperature. The flask was again cooled to -78°C and 60.49 g (0.50 mol) of allyl bromide (1) was added dropwise. The reaction was heated at 45-50°C for 16 hours. The mixture was then filtered to remove AgBr. The filtrate was poured into 100 ml water and the oily layer which formed was washed three times with water and dried over MgSO₄. Distillation gave 79.16 g (3), 76.1%, bp 120-121°C. The identity of the product was confirmed using ¹H NMR spectroscopy (¹H NMR (CDCl₃/δ): 4.60 (d, 2H, CH₂=CHCH₂O-); 5.34-5.47 (m, 2H, CH₂=CH-); 5.89-5.98 (m, 1H, CH₂=CHCH₂O-)).

(c.) Preparation of (5):

(c.) Preparation of (c):

In a high pressure reactor, 72.05 g (0.35 mol) of (3), 80.53 g (0.70 mol) dichloromethylsilane (4) and 0.46 g (1.1 mol) catalyst chloroplatinic acid were combined. The reactor was sealed and filled with argon to a pressure of 50 psi (345 kPa) and then heated at 70-90°C for 22 hrs. After cooling to room temperature, the product was then transferred under inert atmosphere to a flask using a double-tip needle. Un-reacted dichloromethylsilane was removed under reduced pressure. Distillation gave 85.89 g (5), 76%, bp 68-71°C/0.80 mm Hg (107 Pa). The identity of the product was confirmed using ^1H NMR spectroscopy (^1H NMR (CDCl_3/δ) : 0.82 (s, 3H, $\text{CH}_3\text{-Si}-$); 1.15-1.25 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2-$); 1.9-2.0 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2-$), 4.1-4.2 (t, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OC}_2\text{F}_4\text{SO}_2\text{F}$).

(d.) Preparation of (6):

(5) (85.8 g, 0.27 mol) was taken up in anhydrous ether (50 mL), and the resultant solution was then added to a mixture of water (50 mL) and ether (50 mL) dropwise under stirring. At the end of the addition, the reaction was allowed to continue overnight. The oily layer was separated from the aqueous layer. The aqueous layer was then extracted with ether (40 mL x 3), and the ether extract was combined with the oily layer product, washed with water until the water phase became neutral to pH paper, dried over anhydrous $MgSO_4$, filtered, and the solvent was removed from the filtrate by rotary evaporator. The resulting colorless liquid residue was further dried at room temperature under 0.1 torr vacuum for 4 hours to yield 70.68 g. cyclosiloxane (6) (99%). The identity of the intermediate (6) was confirmed using 1H NMR spectroscopy (1H NMR ($CDCl_3/8$) : 0.05-0.08 (m, 3H, CH_3Si-); 0.25-0.35 (m, 2H, $SiCH_2CH_2CH_2-$); 1.85-1.90 (broad, 2H, $SiCH_2CH_2O-$) ; 4.0-4.5 (broad, 2H, $SiCH_2CH_2CH_2O$)).

(e.) Preparation of (7):

The cyclosiloxane (**6**) (350 g, 1.305 mol) and hexamethyldisiloxane (42.4 g, 0.261 mol) were added to a round bottom flask with 10 drops of concentrated sulfuric acid and allowed to sit overnight. An additional 10 drops of concentrated sulfuric acid were then added and the mixture was stirred for 24 hours. The mixture was then taken in methylene chloride and washed with water (2 x 500 mL) and then a saturated solution of NaCl containing a small amount of NaHCO₃. The solution was dried over MgSO₄ before removing the solvent by evaporation.

(f.) Preparation of (8):

The sulfonyl fluoride polysiloxane (**7**) (59.80 g, 0.22 mol) was taken up in 270 mL THF. To the THF solution, lithium hydroxide aqueous solution (10.67 g of anhydrous LiOH, 0.44 mol, in 150 mL water) was added dropwise in 6 hours. Theoretically, two moles of lithium hydroxide are required to convert each sulfonyl fluoride group to lithium sulfonate. However, lithium hydroxide readily absorbs moisture because it is hygroscopic. A slight excess of LiOH was added until the solution became neutral using a pH meter as a monitor. The absence of ^{19}F NMR absorption at 123.5 ppm due to $-\text{SO}_2\text{F}$ confirmed that all of the sulfonyl fluoride groups were converted to lithium

sulfonate. THF and water were then rotary evaporated off. The residual white solid was dried at 50°C under 0.1 torr (13 Pa) vacum overnight.

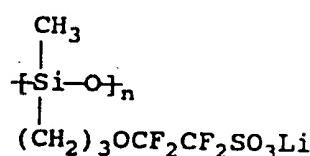
The resulting crude product was dissolved in 200 mL acetone. The mixture was filtered in order to remove LiF, and the filtrate was then concentrated. The concentrated acetone solution was added dropwise to 600 mL of dry ether under stirring. The polymer product was precipitated out. The polymer product (8) was then dried at 70-80°C under 0.05 torr (6.5 Pa) vacuum for 2 days, and the pure product (8) was obtained in 93% yield. The identity of the product (8) was confirmed using ¹H NMR spectroscopy (¹H NMR (D₂O/δ): 0.21 (broad, 3H, CH₃Si-); 0.70 (broad, 2H, SiCH₂CH₂CH₂-); 1.80 (broad, 2H, SiCH₂CH₂CH₂-); 4.10 (broad, 2H, SiCH₂CH₂OC₂F₄SO₃Li); ¹⁹F NMR (D₂O/ ppm): -5.61 (s, -CF₂CF₂SO₃Li); -39.03 (s, -CF₂CF₂SO₃Li)).

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Example 2

[0059] A lithium triflate polysiloxane single-ion conducting polymer having the general structure

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was synthesized using the method of the preceding example. The polymer was combined with various plasticizers, and the conductivity σ (Ω⁻¹cm⁻¹) was determined using the method described above. The experimental results thus obtained are set forth in Table I.

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Table I

Plasticizer	Plasticizer Ratio	Ratio of Polymer to Plasticizer	σ (Ω ⁻¹ cm ⁻¹)
12-Crown-4	---	1:3	8.87 E ⁻⁵
PC: EC	1:1	1:3	2.99 E ⁻⁴
PC: DME	1:1	1:3	4.80 E ⁻⁴
EC: DME	1:1	1:3	7.51 E ⁻⁴
EC: DME	2:1	1:3	7.45 E ⁻⁴
EC: MEE	1:2	1:3	5.91 E ⁻⁴
EC: MEE	1:1	1:3	1.06 E ⁻³
EC: MEE	1:1	1:6	1.02 E ⁻³
PC: DEC	1:1	1:3	1.06 E ⁻⁴
PC: DEC	1:1	1:2	9.33 E ⁻⁵
PC: EC: 12-Crown-4	1:1:1	1:3	3.91 E ⁻⁴
PC: EC: DEC	1:1:2	1:3	3.04 E ⁻⁴
DEC: EC: MEE	1:1:2	1:3	6.94 E ⁻⁴
PC: EC: DME	1:1:2	1:2	6.34 E ⁻⁴
PC: EC: DME	1:1:2	1:2.5	8.71 E ⁻⁴
PC: EC: DME	1:1:2	1:3	1.07 E ⁻³
PC: EC: MEE	1:1:2	1:3	1.11 E ⁻³
PC: EC: MEE	1:1:2	1:3.5	5.24 E ⁻⁴
PC: EC: MEE	1:1:2	1:4	4.32 E ⁻⁴

[0060] In Table I, the abbreviations are as follows: PC, propylene carbonate; EC, ethylene carbonate; DME, dimethoxyethane; MEE, methoxyethoxy ethyl ether; and diethylene carbonate. It may be seen that high ambient temperature conductivity may be achieved and varied, if desired, by choosing different plasticizers and/or relative quantities of plasticizer and polymeric electrolyte in the conductive composition.

Example 3

[0061] The polymers set forth in Table II were prepared by copolymerizing the corresponding monomeric species, and then combined with the plasticizers propylene carbonate, ethylene carbonate, and methoxyethoxy ethane and other materials as indicated in Table III. Conductivity data was determined and is set forth in Table III.

Table II

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	NUMBER	SAMPLE
10	SPE1	$(-\text{CH}_2-\underset{\text{CH}_2\text{OC}_2\text{F}_4\text{SO}_3\text{Li}}{\overset{ }{\text{CH}}}-\text{O}-)_n$
15	SPE2	$\begin{array}{c} \text{CH}_3 \\ \\ (-\text{CH}_2-\underset{\text{CH}_2\text{OC}_2\text{F}_4\text{SO}_3\text{Li}}{\overset{ }{\text{C}}}-\text{CH}_2-\text{O}-)_n \end{array}$
20		
25	SPE3	$\begin{array}{c} (-\text{CH}_2-\underset{\text{CH}_2\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OMe}}{\overset{ }{\text{CH}}}-\text{O}-)_{0.2} \xrightarrow{\hspace{1cm}} (-\text{CH}_2-\underset{\text{CH}_2\text{OC}_2\text{F}_4\text{SO}_3\text{Li}}{\overset{ }{\text{CH}}}-\text{O}-)_{0.8} \\ \text{SPE4} \end{array}$
30	SPE4	$\begin{array}{c} (-\text{CH}_2-\underset{\text{CH}_2\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OMe}}{\overset{ }{\text{CH}}}-\text{O}-)_{0.2} \xrightarrow{\hspace{1cm}} (-\text{CH}_2-\underset{\text{CH}_2\text{SO}_3\text{Li}}{\overset{ }{\text{CH}}}-\text{O}-)_{0.8} \\ \text{SPE5} \end{array}$
35	SPE5	$\begin{array}{c} (-\text{CH}_2-\underset{\text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{7.3}\text{Me}}{\overset{ }{\text{CH}}}-\text{O}-)_{0.5} \xrightarrow{\hspace{1cm}} (-\text{CH}_2-\underset{\text{CH}_2\text{SO}_3\text{Li}}{\overset{ }{\text{CH}}}-\text{O}-)_{0.5} \\ \text{SPE6} \end{array}$
40	SPE6	$\begin{array}{c} (-\text{CH}_2-\underset{\text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{7.3}\text{Me}}{\overset{ }{\text{CH}}}-\text{O}-)_{0.5} \xrightarrow{\hspace{1cm}} (-\text{CH}_2-\underset{\text{CH}_2\text{OC}_2\text{F}_4\text{SO}_3\text{Li}}{\overset{ }{\text{CH}}}-\text{O}-)_{0.5} \\ \text{SPE7} \end{array}$
45	SPE7	$\begin{array}{c} \text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_3\text{Li} \\ \\ (-\text{CH}_2-\underset{\text{CO}_2\text{CH}_2\text{CH}_3}{\overset{ }{\text{C}}}-)_x \xrightarrow{\hspace{1cm}} (-\text{CH}_2-\underset{\text{CO}_2(\text{CH}_2)_3\text{CH}_3}{\overset{ }{\text{C}}}-)_y \end{array}$
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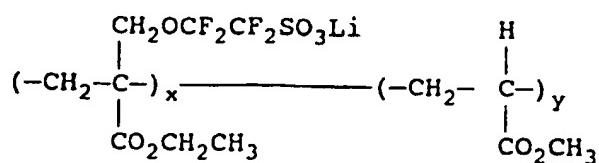
Table II (cont'd.)

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NUMBER SAMPLE

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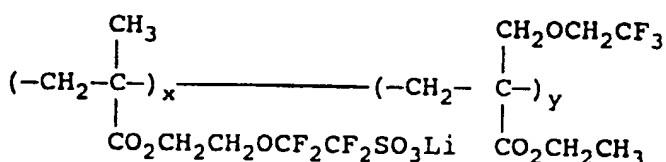
SPE8



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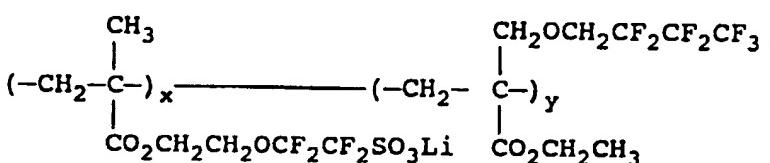
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SPE9



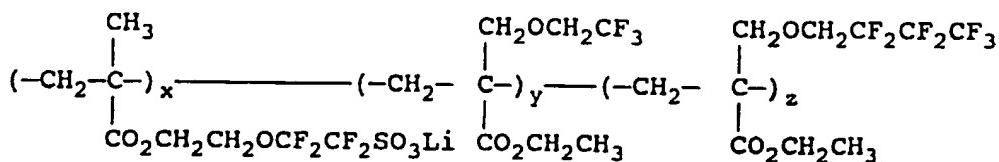
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SPE10



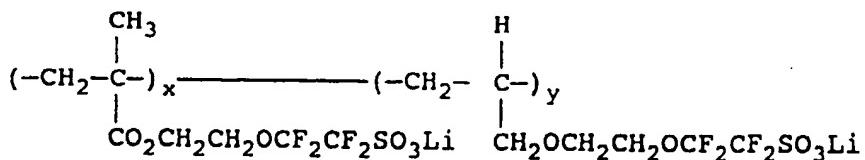
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SPE11



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SPE12



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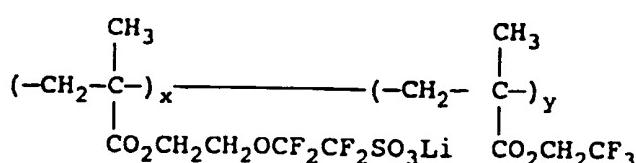
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NUMBER SAMPLE

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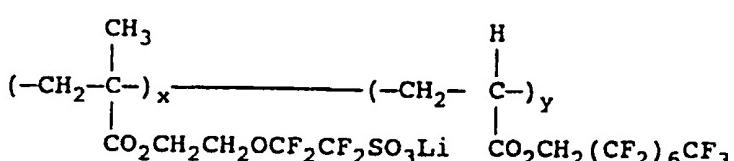
SPE13



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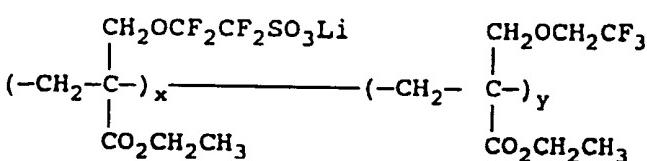
SPE14



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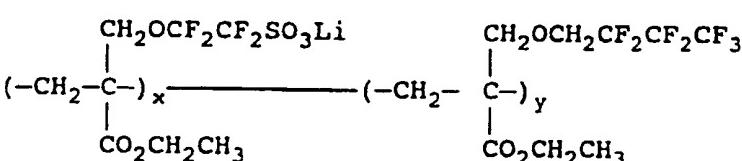
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SPE15



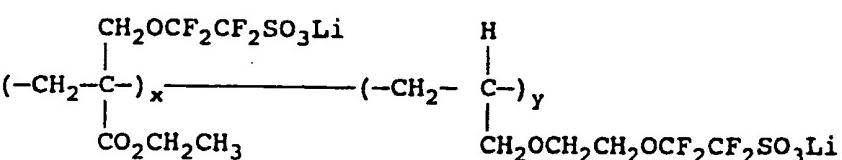
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SPE16



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SPE17



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Table II (cont'd.)

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NUMBER	SAMPLE
10	SPE18
15	$\begin{array}{c} \text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_3\text{Li} \\ \\ (-\text{CH}_2-\text{C}-)_x - (-\text{CH}_2-\text{C}-)_y \\ \\ \text{CO}_2\text{CH}_2\text{CH}_3 \\ \\ \text{CO}_2\text{CH}(\text{CF}_3)_2 \end{array}$
20	SPE19
25	$\begin{array}{c} \text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_3\text{Li} \\ \\ (-\text{CH}_2-\text{C}-)_x - (-\text{CH}_2-\text{C}-)_y \\ \\ \text{CO}_2\text{CH}_2\text{CH}_3 \\ \\ \text{CO}_2\text{CH}_2\text{CF}_3 \end{array}$
30	SPE20
35	$\begin{array}{c} \text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_3\text{Li} \\ \\ (-\text{CH}_2-\text{C}-)_x - (-\text{CH}_2-\text{C}-)_y \\ \\ \text{CO}_2\text{CH}_2\text{CH}_3 \\ \\ \text{CO}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_3 \end{array}$
40	SPE21
45	
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55	

Table III

EXP NO.	SAMPLE	PLASTICIZER	PLASTICIZER RATIO	RATIO OF POLYMER: PLASTICIZER	σ ($\Omega^{-1} \text{ CM}^{-1}$)
1	SPE1	PC:EC	1:1	1:2	8.39×10^{-5}
2	SPE1	PC:EC	1:1	1:3	1.62×10^{-4}
3	SPE1	EC:MEE	1:1	1:3	4.47×10^{-4}
4	SPE1	EC:MEE	1:1	1:4	8.08×10^{-4}
5	SPE1	EC:MEE	1:1	1:4.5	7.57×10^{-4}
6	SPE1	PC:EC:MEE	1:1:2	1:2	3.91×10^{-4}
7	SPE1	PC:EC:MEE	1:1:2	1:3	4.49×10^{-4}
8	SPE1	PC:EC:MEE	1:1:2	1:3.5	5.92×10^{-4}
9	SPE1	PC:EC:MEE	1:1:2	1:4	7.36×10^{-4}
10	SPE1	PC:EC:MEE	1:1:2	1:4.5	7.16×10^{-4}
11	SPE1	PC:EC:MEE	1:1:2	1:5	6.62×10^{-4}
12	SPE2	PC:EC:MEE	1:1:2	1:3	9.80×10^{-5} (~50% soluble)
13	SPE3		1:1:2	1:3	4.22×10^{-4}
14	SPE4		1:1:2	1:3	insoluble
15	SPE5		1:1:2	1:3	insoluble
16	SPE6		1:1:2	1:3	2.17×10^{-4}

Table III (cont'd.)

Copolymer	Copolymer Ratio	Copolymer PC/EC/MEE	σ ($\Omega^{-1} \text{ CM}^{-1}$)	Li Density (wt%)	AIBN (mole%)	Dioxane (wt%)
SPE 7	75:25	1:3	4.14 x 10 ⁻⁴	0.48	0.95	49
SPE 8	75:25	1:3	5.87 x 10 ⁻⁴	0.51	0.96	53
SPE 9	50:50	1:3	4.55 E-4	0.33	1.76	50
SPE 10	75:25 85:15	1:3 1:3	8.54 E-4 4.99 x 10 ⁻⁴	0.42 0.48	1.52 1.05	45 36
SPE 11	35:30:35	1:3	2.20 E-4	0.22	1.41	43
SPE 12	50:50	1:3	4.85 E-4	0.59	0.80	41
SPE 13	50:50	1:3		0.36	1.04	34
SPE 14	50:50			0.23	1.00	36
SPE 15	50:50	1:3 1:4	5.86 E-4 3.62 E-4	0.33 0.27	1.67	49
SPE 16	50:50	1:3 1:4	2.68 E-4 4.21 E-4	0.28 0.22	2.07	49
	75:25	1:3 1:3	2.20 E-4 5.80 E-4	0.42	1.79	44
	(H.MW) 85:15	1:3	4.67 E-4		0.53	0
(w/LiF)						
SPE 17	50:50	1:3	5.57 E-4	0.48 0.59	1.89 1.39	46 52

Table III (cont'd.)

Copolymer	Copolymer Ratio	Copolymer PC/EC/MEE	σ ($\Omega^{-1} \text{ CM}^{-1}$)	Li Density (wt%)	AIBN (mole%)	Dioxane (wt%)
SPE 18	50:50	1.3	5.01 E-4	0.32	1.54	46
SPE 19	50:50	1.3	4.89 E-4	0.36	1.23	45
SPE 20	50:50	1:3	2.56 E-4	0.31	1.00	34
SPE 21	50:50			0.23	1.11	32

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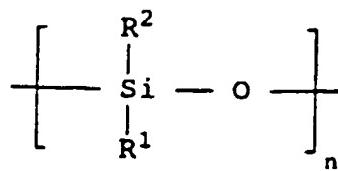
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55 **Claims**

1. A polymer having the structure

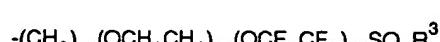
(I)



10 wherein:

R¹ and R² are individually selected from moieties having the structure

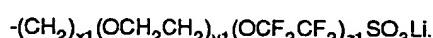
in which R³ is -OM, -N(M)SO₂CF₃ or -C(M)(SO₂CF₃)₂ and M is an alkali metal, or wherein one of R¹ and R² has the structure



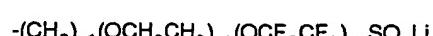
and the other is selected from hydrogen, C₁₋₆ alkyl, fluorinated C₁₋₆ alkyl, C₂₋₆ alkenyl, fluorinated C₂₋₆ alkenyl, aryl, and aralkylene;

25 x1 and z1 may be the same or different and are integers in the range of 1 to 100 inclusive;
y1 is an integer in the range of 0 to 100 inclusive; and
n is an integer indicating the number of mer units in the polymer.

2. The polymer of claim 1 wherein R³ is -OM.
- 30 3. The polymer of claim 1 wherein R³ is -N(M)SO₂CF₃.
4. The polymer of claim 1 wherein R³ is -C(M)(SO₂CF₃)₂.
- 35 5. The polymer of any preceding claim wherein M is lithium.
6. The polymer of claim 2 wherein n is selected to provide the polymer with a weight average molecular weight \bar{M}_w in the range of 10,000 to 3,000,000.
- 40 7. The polymer of claim 6 wherein n is selected to provide the polymer with a weight average molecular weight \bar{M}_w in the range of 100,000 to 1,000,000.
8. The polymer of claim 1 wherein R¹ and R² are the same moiety having the structure



9. The polymer of claim 1 wherein R¹ is a moiety having the structure



and R² is a moiety selected from hydrogen, C₁₋₆ alkyl, fluorinated C₁₋₆ alkyl, C₂₋₆ alkenyl, fluorinated C₂₋₆ alkenyl, aryl and aralkylene.

- 55 10. The polymer of claim 1 wherein R¹ and R² are the same moiety having the structure



11. The polymer of claim 1 wherein R¹ is a moiety having the structure



10 and R² is a moiety selected from hydrogen, C₁₋₆ alkyl, fluorinated C₁₋₆ alkyl, C₂₋₆ alkenyl, fluorinated C₂₋₆ alkenyl, aryl and aralkylene.

12. The polymer of claim 1 wherein R¹ and R² are the same moiety having the structure

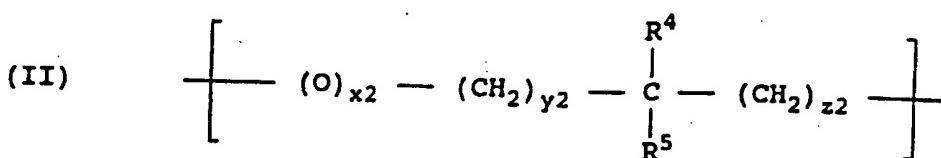


13. The polymer of claim 1 wherein R¹ is a moiety having the structure

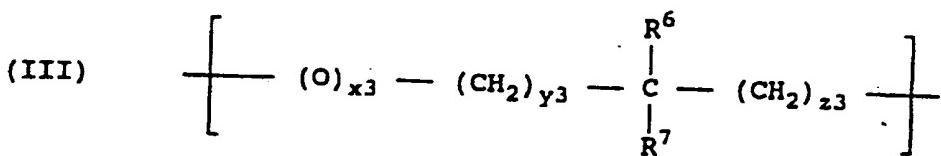


20 and R² is a moiety selected from hydrogen, C₁₋₆ alkyl fluorinated C₁₋₆ alkyl, C₂₋₆ alkenyl, fluorinated C₂₋₆ alkenyl, aryl and aralkylene.

25 14. A copolymer comprising first mer units having the structure



35 and second mer units having the structure



45 wherein:

R⁴ and R⁶ are independently selected from hydrogen, C₁₋₆ alkyl, C₁₋₆ alkoxy, -COOR⁸ and -(CH₂)_{n1}-O-R⁸ in which R⁸ is C₁₋₆ alkyl or fluorinated C₁₋₆ alkyl and n1 is an integer in the range of 1 to 6 inclusive; R⁵ is -(CH₂)_{x4}(OCH₂CH₂)_{y4}(OCF₂CF₂)_{z4}SO₃M in which M is an alkali metal; R⁷ is -(CH₂)_{x5}(OCH₂CH₂)_{y5}OCH₃ or -COOR⁹ in which R⁹ is C₁₋₆ alkyl or fluorinated C₁₋₆ alkyl; and x2, x3, x4, x5, y2, y3, y4, y5, z2, z3 and z4 may be the same or different and are integers in the range of 1 to 100 inclusive.

55 15. The copolymer of claim 14 wherein M is lithium.

16. The copolymer of claim 15 having a weight average molecular weight \bar{M}_w in the range of 10,000 to 3,000,000.

17. The copolymer of claim 16 having a weight average molecular weight \bar{M}_w in the range of 100,000 to 1,000,000.

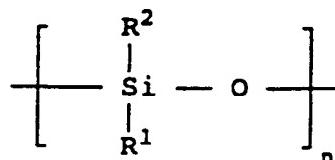
18. The copolymer of claim 14 wherein R⁴ and R⁶ are independently selected from hydrogen and C₁₋₆ alkyl, and R⁷ is -(CH₂)_{x4}(OCH₂CH₂)_{y4}OCH₃.

5 19. The copolymer of claim 14 wherein R⁴ and R⁷ may be the same or different, and are selected from moieties having the structure -COOR⁸, and R⁶ is hydrogen or C₁₋₆ alkyl.

20. A composition having enhanced ambient temperature conductivity comprising:

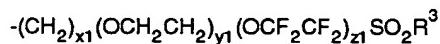
10 (a) a single-ion conducting polymer having the structure

15 (I)

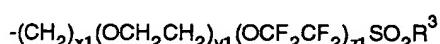


20 wherein:

25 R¹ and R² are individually selected from moieties having the structure



in which R³ is -OM, N(M)SO₂CF₃ or C(M)(SO₂CF₃)₂ and M is an alkali metal, or wherein one of R₁ and R₂ has the structure



30 and the other is selected from hydrogen, C₁₋₆ alkyl, fluorinated C₁₋₆ alkyl, C₂₋₆ alkenyl, fluorinated C₂₋₆ alkenyl, aryl and aralkylene,

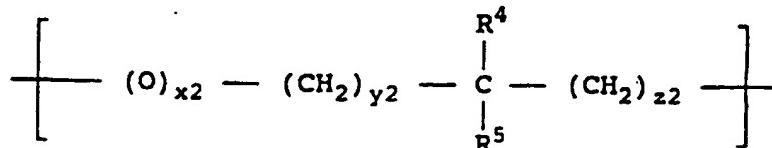
35 x1 and z1 may be the same or different and are integers in the range of 1 to 100 inclusive, y1 is an integer in the range of 0 to 100 inclusive, and n is an integer indicating the number of mer units in the polymer; and

40 (b) a plasticizer selected from C₁₋₆ alkyl carbonates, glymes and cyclic ethers, in an amount effective to enhance the ionic conductivity of the copolymer.

21. A composition having enhanced ambient temperature conductivity comprising:

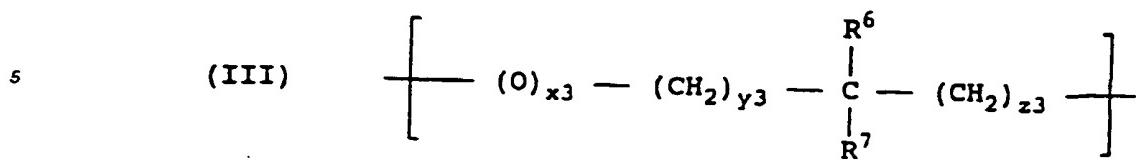
45 (a) a single-ion conducting polymer electrolyte in the form of a polymer containing first mer units having the structure

50 (II)



55

and second mer units having the structure



10 wherein:

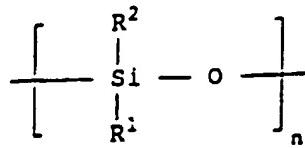
15 R⁴ and R⁶ are independently selected from hydrogen, C₁₋₆ alkyl, C₁₋₆ alkoxy, -COOR⁸ and -(CH₂)_{n1}-O-R⁸ in which R⁸ is C₁₋₆ alkyl or fluorinated C₁₋₆ alkyl and n1 is an integer in the range of 1 to 6 inclusive; R⁵ is -(CH₂)_{x4}(OCH₂CH₂)_{y4}(OCF₂CF₂)_{z4}SO₃M in which M is an alkali metal; R⁷ is -(CH₂)_{x5}(OCH₂CH₂)_{y5}OCH₃ or -COOR⁹ in which R⁹ is C₁₋₆ alkyl or fluorinated C₁₋₆ alkyl; and x2, x3, x4, x5, y2, y3, y4, y5, z2, z3 and z4 may be the same or different and are integers in the range of 1 to 100 inclusive; and

Patentansprüche

- ## 1. Polymer der Struktur

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(I)



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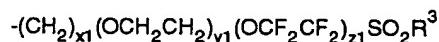
worin

R¹ und R² einzeln unter Resten der Struktur

15

ausgewählt sind, worin R³ -OM, -N(M)SO₂CF₃ oder -C(M)(SO₂CF₃)₂ ist und M ein Alkalimetall ist, oder worin eine der Gruppen R¹ und R² die Struktur

20



hat und die andere unter Wasserstoff, C₁₋₆-Alkyl, fluoriertem C₁₋₆-Alkyl, C₂₋₆-Alkenyl, fluoriertem C₂₋₆-Alkenyl, Aryl und Aralkylen ausgewählt ist,

25

x1 und z1 gleich oder verschieden sein können und ganze Zahlen im Bereich von 1 bis 100 einschließlich sind,

y1 eine ganze Zahl im Bereich von 0 bis 100 einschließlich ist und

30

n eine ganze Zahl ist, die die Anzahl von mer-Einheiten in dem Polymer angibt.

2. Polymer nach Anspruch 1, worin R³ -OM ist.

3. Polymer nach Anspruch 1, worin R³ -N(M)SO₂CF₃ ist.

35

4. Polymer nach Anspruch 1, worin R³ -C(M)(SO₂CF₃)₂ ist.

5. Polymer nach einem der vorausgehenden Ansprüche, worin M Lithium ist.

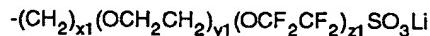
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6. Polymer nach Anspruch 2, worin n so ausgewählt ist, daß das Polymer ein mittleres Molekulargewicht (Gewichtsmittel) \bar{M}_w im Bereich von 10 000 bis 3 000 000 bekommt.

7. Polymer nach Anspruch 6, worin n so ausgewählt ist, daß das Polymer ein mittleres Molekulargewicht (Gewichtsmittel) \bar{M}_w im Bereich von 100 000 bis 1 000 000 bekommt.

45

8. Polymer nach Anspruch 1, worin R¹ und R² der gleiche Rest mit der Struktur



50 sind.

9. Polymer nach Anspruch 1, worin R¹ ein Rest der Struktur



ist und R² ein Rest ist, der unter Wasserstoff, C₁₋₆-Alkyl, fluoriertem C₁₋₆-Alkyl, C₂₋₆-Alkenyl, fluoriertem C₂₋₆-Alkenyl, Aryl und Aralkylen ausgewählt ist.

10. Polymer nach Anspruch 1, worin R¹ und R² der gleiche Rest der Struktur



5

sind.

11. Polymer nach Anspruch 1, worin R¹ ein Rest der Struktur

10

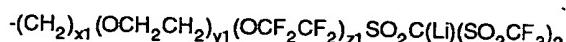


ist und R² ein Rest ist, der unter Wasserstoff, C₁₋₆-Alkyl, fluoriertem C₁₋₆-Alkyl, C₂₋₆-Alkenyl, fluoriertem C₂₋₆-Alkenyl, Aryl und Aralkylen ausgewählt ist.

15

12. Polymer nach Anspruch 1, worin R¹ und R² der gleiche Rest mit der Struktur

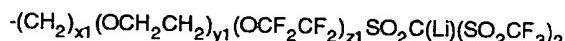
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sind.

13. Polymer nach Anspruch 1, worin R¹ ein Rest der Struktur

25

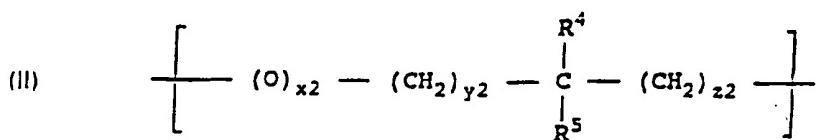


ist und R² ein Rest ist, der unter Wasserstoff, C₁₋₆-Alkyl, fluoriertem C₁₋₆-Alkyl, C₂₋₆-Alkenyl, fluoriertem C₂₋₆-Alkenyl, Aryl und Aralkylen ausgewählt ist.

30

14. Copolymer mit ersten mer-Einheiten mit der Struktur

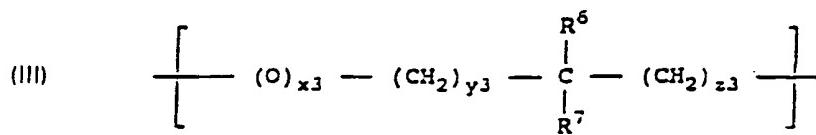
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40

und zweiten mer-Einheiten mit der Struktur

45



50

worin R⁴ und R⁶ unabhängig voneinander unter Wasserstoff, C₁₋₆-Alkyl, C₁₋₆-Alkoxy, -COOR⁸ und -(CH₂)_{n1}-O-R⁸ ausgewählt sind, worin R⁸ C₁₋₆-Alkyl oder fluoriertes C₁₋₆-Alkyl ist und n1 eine ganze Zahl im Bereich von 1 bis 6 einschließlich ist,

55

R⁵-(CH₂)_{x4}(OCH₂CH₂)_{y4}(OCF₂CF₂)_{z4}SO₃M ist, worin M ein Alkalimetall ist,

R⁷-(CH₂)_{x5}(OCH₂CH₂)_{y5}OCH₃ oder -COOR⁹ ist, worin R⁹ C₁₋₆-Alkyl oder fluoriertes C₁₋₆-Alkyl ist und

x2, x3, x4, x5, y2, y3, y4, y5, z2, z3 und z4 gleich oder verschieden sein können und ganze Zahlen im Bereich

von 1 bis 100 einschließlich sind.

15. Copolymer nach Anspruch 14, worin M Lithium ist.

5 16. Copolymer nach Anspruch 15 mit einem mittleren Molekulargewicht (Gewichtsmittel) \bar{M}_w im Bereich von 10 000 bis 3 000 000.

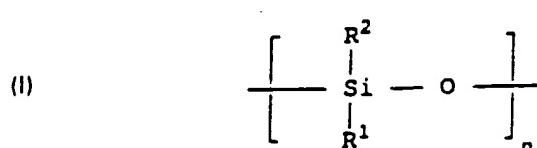
17. Copolymer nach Anspruch 16 mit einem mittleren Molekulargewicht (Gewichtsmittel) \bar{M}_w im Bereich von 100 000 bis 1 000 000.

10 18. Copolymer nach Anspruch 14, worin R⁴ und R⁶ unabhängig voneinander unter Wasserstoff und C₁₋₆-Alkyl ausgewählt sind und R⁷ -(CH₂)_{x4}(OCH₂CH₂)_{y4}OCH₃ ist.

15 19. Copolymer nach Anspruch 14, worin R⁴ und R⁷ gleich oder verschieden sein können und unter Resten mit der Struktur -COOR⁸ ausgewählt sind und R⁶ Wasserstoff oder C₁₋₆-Alkyl ist.

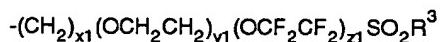
20. Zusammensetzung mit verbesserter Leitfähigkeit bei Umgebungstemperatur mit

a) einem Einzelion leitenden Polymer mit der Struktur

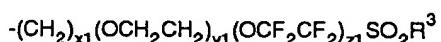


worin

30 R¹ und R² einzeln unter Resten mit der Struktur



ausgewählt sind, worin R³ -OM, -N(M)SO₂CF₃ oder -C(M)(SO₂CF₃)₂ ist und M ein Alkalimetall ist, oder worin eine der Gruppen R¹ und R² die Struktur



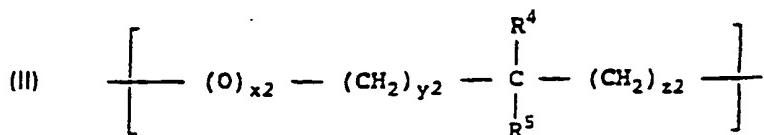
45 hat und die andere unter Wasserstoff, C₁₋₆-Alkyl, fluoriertem C₁₋₆-Alkyl, C₂₋₆-Alkenyl, fluoriertem C₂₋₆-Alkenyl, Aryl und Aralkylen ausgewählt ist, x1 und z1 gleich oder verschieden sein können und ganze Zahlen im Bereich von 1 bis 100 einschließlich sind, y1 eine ganze Zahl im Bereich von 0 bis 100 einschließlich ist und n eine ganze Zahl ist, die die Anzahl der mer-Einheiten in dem Polymer angibt, und

b) einem Weichmacher, der unter C₁₋₆-Alkylcarbonaten, Glymen und zyklischen Ethern ausgewählt ist, in einer wirksamen Menge, um Ionenleitfähigkeit des Polymers zu verbessern.

50 21. Zusammensetzung mit verbesserter Leitfähigkeit bei Umgebungstemperatur mit

a) einem Einzelion leitenden Polymerelektrolyten in der Form eines Polymers, welches erstens mer-Einheiten der Struktur

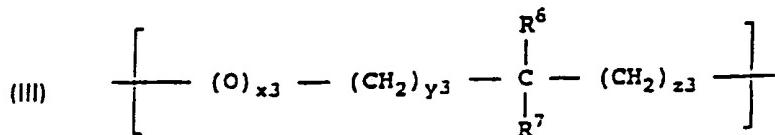
5



10

und zweitens mer-Einheiten der Struktur

15



20

enthält, worin R⁴ und R⁶ unabhängig voneinander unter Wasserstoff, C₁₋₆-Alkyl, C₁₋₆-Alkoxy, -COOR⁸ und -(CH₂)_{n1}-O-R⁸ ausgewählt sind, worin R⁸ C₁₋₆-Alkyl oder fluoriertes C₁₋₆-Alkyl ist und n1 eine ganze Zahl im Bereich von 1 bis 6 einschließlich ist,

R⁵-(CH₂)_{x4}(OCH₂CH₂)_{y4}(OCF₂CF₂)_{z4}SO₃M ist, worin M ein Alkalimetall ist,

25

R⁷-(CH₂)_{x5}(OCH₂CH₂)_{y5}OCH₃ oder -COOR⁹ ist, worin R⁹ C₁₋₆-Alkyl oder fluoriertes C₁₋₆-Alkyl ist und

x2, x3, x4, x5, y2, y3, y4, y5, z2, z3 und z4 gleich oder verschieden sein können und ganze Zahlen im Bereich von 1 bis 100 einschließlich sind und

30

b) einem Weichmacher, der unter C₁₋₆-Alkylcarbonaten, Glymen und zyklischen Ethern ausgewählt ist, in einer wirksamen Menge, um die Ionenleitfähigkeit in dem Copolymer zu verbessern.

22. Zusammensetzung nach Anspruch 20 oder 21 in der Form eines Filmes.

23. Einzelion leitende Gelelektrolytfilmzusammensetzung mit verbesserter Leitfähigkeit bei Umgebungstemperatur und verbesserter mechanischer Festigkeit mit

a) dem Polymer nach Anspruch 1 oder 14,

40

b) einem Weichmacher, der unter linearen Carbonaten, Glymen, zyklischen Ethern und Kombinationen hiervon ausgewählt ist,

45

c) einer Menge eines Verstärkungsmaterials, das wirksam ist, die mechanische Festigkeit der Filmzusammensetzung zu verbessern.

24. Zusammensetzung nach Anspruch 23, worin das verstärkende Material Polyvinylidenfluorid ist.

50

25. Verfahren zur Herstellung eines Einzelion leitenden Gelelektrolytfilms mit ausgewählter Filmdicke mit den Stufen, in denen man

a) eine Gelelektrolytzusammensetzung bildet, indem man

i) das Einzelion leitende Polymer nach Anspruch 1 oder 14 mit

55

ii) einer wirksamen Weichmachermenge, um die Ionenleitfähigkeit dieses Polymers zu verbessern, und

iii) einer wirksamen Menge eines Verstärkungsmaterials, um die mechanische Festigkeit zu verbessern, vereinigt,

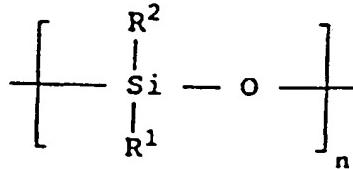
- b) die resultierende Zusammensetzung auf eine wirksame Temperatur und während einer wirksamen Zeit, um eine Fluidlösung zu bilden, erhitzt,
 5 c) die Fluidlösung zwischen zwei festen Substraten preßt, um einen Film einer erwünschten Dicke zu bilden,
 d) den Film kühl und
 e) den Film von den festen Substraten trennt.

- 10 26. Verfahren nach Anspruch 25, bei dem das Verstärkungsmaterial Polyvinyldenfluorid ist.
 27. Batterie in festem Zustand mit einer positiven Elektrode, einer negativen Elektrode und dem Einzelion leitenden Polymerelektrolyten nach Anspruch 1 oder 14.

15 **Revendications**

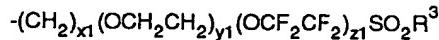
20 1. Polymère ayant la structure

(I)

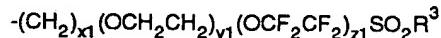


25 dans laquelle :

30 R^1 et R^2 sont choisis individuellement parmi des fragments ayant la structure



35 dans laquelle R^3 est -OM, -N(M)SO₂CF₃ ou -C(M)(SO₂CF₃)₂ et M est un métal alcalin, ou dans laquelle l'un de R¹ et R² a la structure



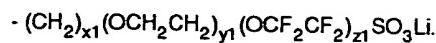
40 et l'autre est choisi parmi l'hydrogène, des groupes alkyle en C₁₋₆, alkyle fluoré en C₁₋₆, alcényle en C₂₋₆, alcényle fluoré en C₂₋₆, aryle et aralkylène ;
 x1 et z1 peuvent être identiques ou différents et sont des nombres entiers valant de 1 à 100 inclus ;
 y1 est un nombre entier valant de 0 à 100 inclus ; et
 45 n est un nombre entier indiquant le nombre d'unités "mère" dans le polymère.

2. Polymère selon la revendication 1, dans lequel R³ est -OM.
 3. Polymère selon la revendication 1, dans lequel R³ est -N(M)SO₂CF₃.
 50 4. Polymère selon la revendication 1, dans lequel R³ est -C(M)(SO₂CF₃)₂.
 5. Polymère selon l'une quelconque des revendications précédentes, dans lequel M est le lithium.
 55 6. Polymère selon la revendication 2, dans lequel n est choisi de façon à conférer au polymère un poids moléculaire moyen en poids \bar{M}_w compris entre 10 000 et 3 000 000.
 7. Polymère selon la revendication 6, dans lequel n est choisi de façon à conférer au polymère un poids moléculaire

moyen en poids \bar{M}_w compris entre 100 000 et 1 000 000.

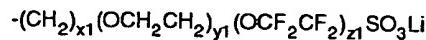
8. Polymère selon la revendication 1, dans lequel R¹ et R² sont le même fragment ayant la structure

5



9. Polymère selon la revendication 1, dans lequel R¹ est un fragment ayant la structure

10



et R² est un fragment choisi parmi l'hydrogène, des groupes alkyle en C₁₋₆, alkyle fluoré en C₁₋₆, alcényle en C₂₋₆, alcényle fluoré en C₂₋₆, aryle et aralkylène.

15

10. Polymère selon la revendication 1, dans lequel R¹ et R² sont le même fragment ayant la structure

20



25

11. Polymère selon la revendication 1, dans lequel R¹ est un fragment ayant la structure



25

et R² est un fragment choisi parmi l'hydrogène, des groupes alkyle en C₁₋₆, alkyle fluoré en C₁₋₆, alcényle en C₂₋₆, alcényle fluoré en C₂₋₆, aryle et aralkylène.

30

12. Polymère selon la revendication 1, dans lequel R¹ et R² sont le même fragment ayant la structure



35

13. Polymère selon la revendication 1, dans lequel R¹ est un fragment ayant la structure



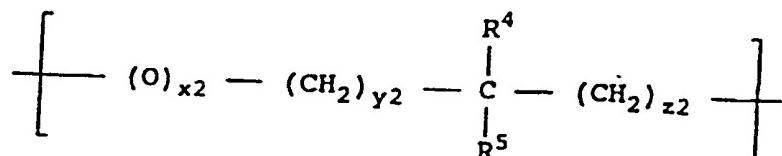
40

et R² est un fragment choisi parmi l'hydrogène, des groupes alkyle en C₁₋₆, alkyle fluoré en C₁₋₆, alcényle en C₂₋₆, alcényle fluoré en C₂₋₆, aryle et aralkylène.

14. Copolymère comprenant des premières unités -mère ayant la structure

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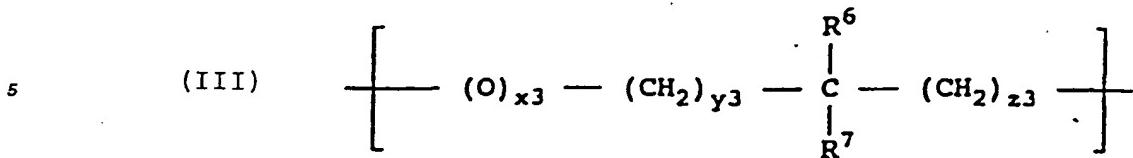
(II)



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et des secondes unités -mère ayant la structure

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10 dans lesquelles :

R⁴ et R⁶ sont choisis indépendamment l'un de l'autre parmi l'hydrogène, des groupes alkyle en C₁₋₆, alkoxy en C₁₋₆, -COOR⁸ et -(CH₂)_n-O-R⁸ où R⁸ est un groupe alkyle en C₁₋₆ ou alkyle fluoré en C₁₋₆, et nI est un nombre entier valant de 1 à 6 inclus ;

R⁵ est -(CH₂)₄(OCH₂CH₃)₄(OCF₂CF₃)₄SO₃M où M est un métal alcalin :

R⁷ est -(CH₂)_{x5}(OCH₂CH₂)_{y5}OCH₃ ou -COOR⁹ où R⁹ est un groupe alkyle en C₁₋₆ ou alkyle fluoré en C₁₋₆ ; et x2, x3, x4, x5, y2, y3, y4, y5, z2, z3 et z4 peuvent être identiques ou différents et sont des nombres entiers valant de 1 à 100 inclus.

20 15. Copolymère selon la revendication 14, dans lequel M est le lithium.

16. Copolymère selon la revendication 15, ayant un poids moléculaire moyen en poids \bar{M}_w compris entre 10 000 et 3 000 000.

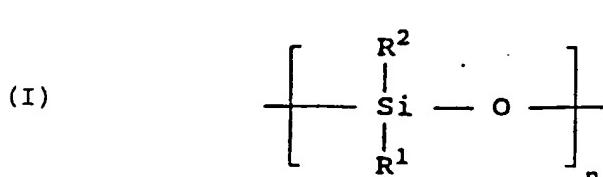
25 17. Copolymère selon la revendication 16, ayant un poids moléculaire moyen en poids \bar{M}_w compris entre 100 000 et 1 000 000.

18. Copolymère selon la revendication 14, dans lequel R⁴ et R⁶ sont choisis indépendamment l'un de l'autre parmi l'hydrogène et des groupes alkyle en C₁₋₆, et R⁷ est -(CH₂)_n(OCH₂CH₂)_mOCH₃.

30 19. Copolymère selon la revendication 14, dans lequel R⁴ et R⁷ peuvent être identiques ou différents et sont choisis parmi des fragments ayant la structure -COOR⁸, et R⁶ est l'hydrogène ou un groupe alkyle en C₁₋₆.

20. Composition ayant une conductivité augmentée à la température ambiante, comprenant :

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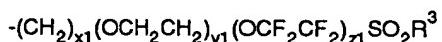


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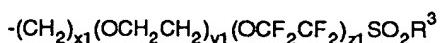
dans laquelle :

R^1 et R^2 sont choisis individuellement parmi des fragments ayant la structure

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55 dans laquelle R³ est -OM, -N(M)SO₂CF₃ ou C(M)(SO₂CF₃)₂ et M est un métal alcalin, ou dans laquelle l'un de R¹ et R² a la structure



et l'autre est choisi parmi l'hydrogène, des groupes alkyle en C₁₋₆, alkyle fluoré en C₁₋₆, alcényle en C₂₋₆, alcényle fluoré en C₂₋₆, aryle et aralkylène, x₁ et z₁ peuvent être identiques ou différents et sont des nombres entiers valant de 1 à 100 inclus, y₁ est un nombre entier valant de 0 à 100 inclus, et n est un nombre entier indiquant le nombre d'unités -mère dans le polymère ; et

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(b) un plastifiant choisi parmi des carbonates d'alkyle en C₁₋₆, des glymes et des éthers cycliques, en une quantité efficace pour augmenter la conductivité ionique du copolymère.

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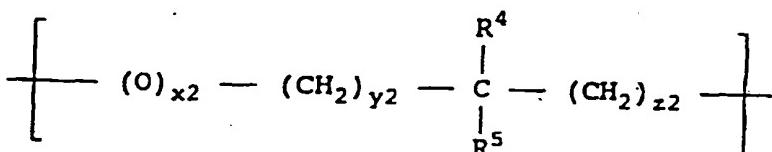
21. Composition ayant une conductivité augmentée à la température ambiante, comprenant :

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(a) un électrolyte polymère conducteur d'ion unique sous la forme d'un polymère contenant des premières unités mère ayant la structure

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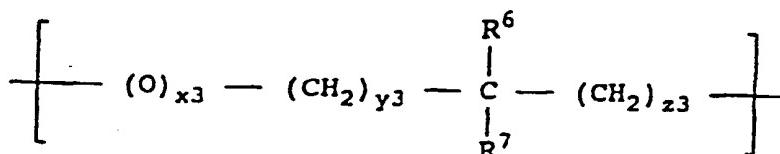
(II)



et des secondes unités -mère ayant la structure

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(III)



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dans lesquelles :

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R⁴ et R⁶ sont choisis indépendamment l'un de l'autre parmi l'hydrogène, des groupes alkyle en C₁₋₆, alkoxy en C₁₋₆, -COOR⁸ et -(CH₂)_{n1}-O-R⁸ où R⁸ est un groupe alkyle en C₁₋₆ ou alkyle fluoré en C₁₋₆, et n₁ est un nombre entier valant de 1 à 6 inclus ;

R⁵ est -(CH₂)_{x4}(OCH₂CH₂)_{y4}(OCF₂CF₂)_{z4}SO₃M où M est un métal alcalin ;

R⁷ est -(CH₂)_{x5}(OCH₂CH₂)_{y5}OCH₃ ou -COOR⁹ où R⁹ est un groupe alkyle en C₁₋₆ ou alkyle fluoré en C₁₋₆ ; et

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x₂, x₃, x₄, x₅, y₂, y₃, y₄, y₅, z₂, z₃ et z₄ peuvent être identiques ou différents et sont des nombres entiers valant de 1 à 100 inclus ; et

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(b) un plastifiant choisi parmi des carbonates d'alkyle en C₁₋₆, des glymes et des éthers cycliques, en une quantité efficace pour augmenter la conductivité ionique du copolymère.

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22. Composition selon la revendication 20 ou la revendication 21 sous la forme d'un film.

23. Composition en forme de film d'électrolyte à base de gel conducteur d'ion unique ayant une conductivité et une résistance mécanique augmentées à la température ambiante, comprenant :

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(a) le polymère selon la revendication 1 ou la revendication 14 ;

(b) un plastifiant choisi parmi des carbonates linéaires, des glymes, des éthers cycliques et des combinaisons de ceux-ci ; et

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(c) une matière de renfort en une quantité efficace pour augmenter la résistance mécanique de la composition sous la forme d'un film.

24. Composition selon la revendication 23, dans laquelle la matière de renfort est du fluorure de polyvinylidène.

25. Procédé de fabrication d'un film d'électrolyte à base de gel conducteur d'ion unique, ayant une épaisseur de film choisie, comprenant les étapes consistant à :

(a) former une composition d'électrolyte à base de gel en combinant (i) le polymère conducteur d'ion unique selon la revendication 1 ou la revendication 14 avec (ii) un plastifiant en une quantité efficace pour augmenter la conductivité ionique dudit polymère et (iii) une matière de renfort en une quantité efficace pour augmenter la résistance mécanique ; (b) chauffer la composition résultante à une température et pendant une durée efficaces pour former une solution fluide ; (c) comprimer la solution fluide entre deux substrats solides pour former un film ayant une épaisseur désirée ; (d) refroidir le film ; et (e) séparer le film des substrats solides.

26. Procédé selon la revendication 25, dans lequel la matière de renfort est du fluorure de polyvinylidène.

27. Batterie à état solide comprenant une électrode positive, une électrode négative et l'électrolyte polymère conducteur d'ion unique selon la revendication 1 ou la revendication 14.

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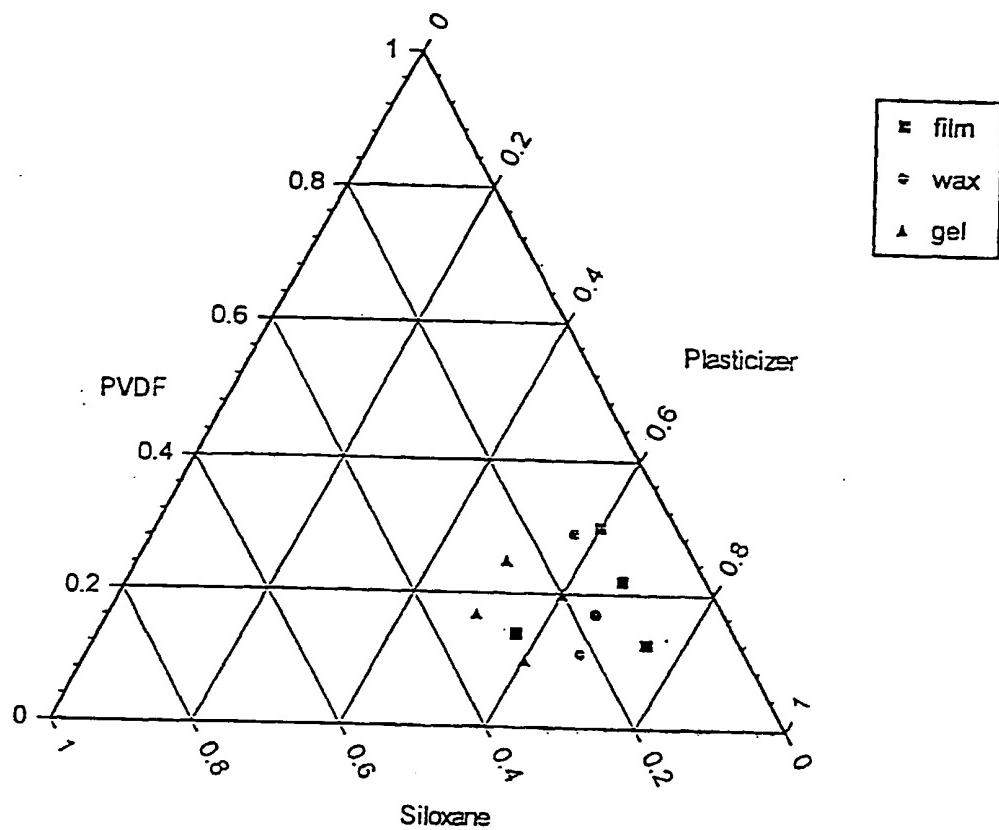


FIG. 1